Synthesis, Characterization and catalytic application of polyphosphoric acid-Zr-pillared clay for the multicomponent synthesis of tetrahydropyridines.

A Dissertation

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DECLARATION

The work embodied in this report is an original investigation carried out by the author, on the topic entitled, **"*Synthesis, Characterization and catalytic application of polyphosphoric acid-Zr-pillared clay for the multicomponent synthesis of tetrahydropyridines*"**, *for partial fulfilment of degree in Master of Science (Chemistry), NIT Rourkela. To the best of my knowledge and belief, this work has not been submitted to any other University or Institution to confer any Degree or Diploma.*

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CERTIFICATE

This is to certify that the dissertation entitled, "**Synthesis Characterization and catalytic application of polyphosphoric acid-Zr-pillared clay for the multicomponent synthesis of tetrahydropyridines**", being submitted by Ratikanta Sahoo and Sushree Sweta Leena, to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha for partial fulfilment of the Master degree in Science (Chemistry) is a record of bonafide research work carried out under my guidance and supervision. The project report has not been submitted by them for any other degree to any other Institution or University. I am satisfied that the dissertation has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

Prof. B.G Mishra
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CHAPTER 1

INTRODUCTION TO THE CLAY MATERIALS

1.1 General Introduction

Clays are the most common minerals on earth's surface and have been used by man for centuries. These materials have wide range of applications in different areas. Clays are employed as raw materials for building ceramics, paper coating and filling, drilling mud, foundry moulds, and pharmaceuticals. These materials find applications as adsorbents and catalysts for various industrial applications [1]. Clay minerals help in removal of toxic organic chemicals such as chlorinated compounds, heavy metal ions (eg. Pb^{2+}, Hg^{2+}) and nuclear waste from aqueous sources by the adsorption process [2,3]. Acid treated clays are employed for cracking of heavy fraction of the crude oil [4]. Several organic transformation reactions are carried out using salt loaded, acid-treated and ion exchanged clays as catalysts [1,5,6]. Classification of clays is done mainly on the basis of type of ions present in the interlayer spacing. The clay materials have been broadly classified as cationic and anionic clays [6]. The cationic clays have abundance availability in nature and contain negatively charged alumino-silicate layers. Cations present in the interlayer space of these clays balance the negative charge. The presence of structural hydroxyl groups contribute towards surface acidic properties of the clays. Work described in this thesis is based on structural modification of cationic clay and its application towards catalysis.

1.2 Structural features of clay materials

Clays are two dimensional hydrous layer silicates belonging to the phyllosillicate family [7]. The extremely stable SiO_4 tetrahedral units undergo condensation to form silicate layers that form basic framework of the clay. The SiO_4 tetrahedra share three basal oxygen atoms by corner sharing to from the silicate layer. The structure of a typical silicate plane is shown in the Fig. 1.1

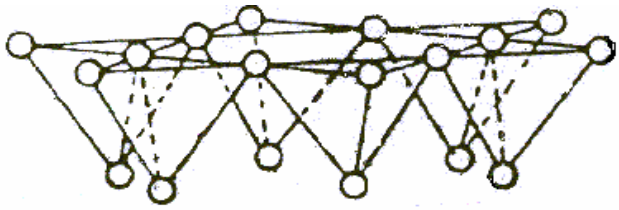


Fig.1.1. Silicate sheet of a clay mineral

Each tetrahedron in the silicate layer comprises of a spare oxygen atom which condense with octahedral planar units to from different classes of clay materials. MO_6 (M= Al, Mg etc.) octahedra are the fundamental unit of the octahedral layer. The MO_6octahedra are polymerized by sharing its four edges to form the octahedral layer [7]. The octahedral layer is shown in fig 1.2.

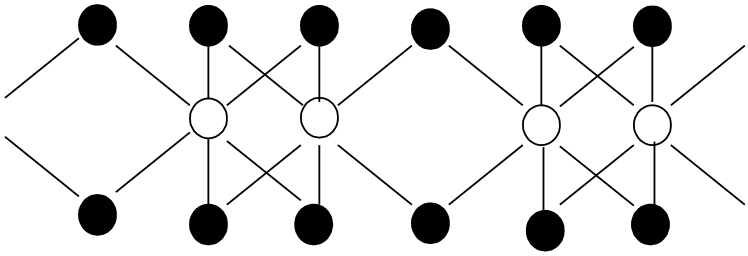


Fig.1.2. Alumina octahedral sheets in clay mineral

The most widely used clay material in catalysis is montmorillonite. The structure of Montmorillonite consists of clay sheets. Each clay sheet comprises of an alumina layer condensed with two-silicate layers. These clay sheets are stacked in z direction to form the clay mineral structure. The structure of montmorillonite clay is shown in fig 1.3.

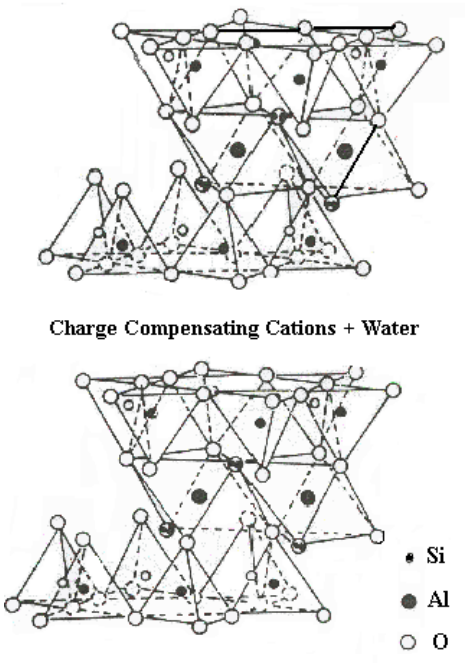


Fig.1.3. Structure of 2:1 clay mineral montmorillonite

The space in between two clay sheet is called the interlayer spacing. Negative charge in the clay sheet is developed due to the isomorphic substitution of the of Al^{3+} ion by lower valent ions such as Fe^{2+}, Mg^{2+} in the octahedral layer of clay sheet.The total amount of negative charge resulted due to isomorphous substitutions is called the cation exchange capacity (CEC) of the clay material [8]. This negative charge is balanced by the charge compensating cations present in the interlayer spacings. The charge compensating cations include alkali and alkaline earth metal ions which are easily exchangeable with the other cationic species.

1.3 Acid properties of the clay

Cationic clays play vital role as solid acid catalyst to carry out several organic transformation reactions. Mainly Brønsted acidity is observed in the clay materials. However, Lewis acidity can be generated by suitable thermal treatment [1,2]. On subjecting clay minerals to high

temperature, Al^{3+} ions get exposed at the broken crystallite edges [2]. Lewis acidity is likely to be associated with these sites

Under the influence of ”negative” potential of the clay sheet the highly polarized and sterically hindered water molecules present in the primary coordination sphere of the interlayer ion dissociate to form protons which act as a source of Brønsted acidity. Presence of structural hydroxyl groups in the octahedral layers act as another source of acidity.

1.4 Disadvantages of clay materials as catalysts

Although clay materials are used as solid acid catalysts for variety of organic reactions, they possess certain inherent disadvantages, which limit their application in heterogeneous catalysis [9]. At high temperature extensive dehydration of the clay sheets and complete collapse of clay structure takes place. This leads to loss Brønsted acidity. Thus at higher temperature their applications are limited. The interlayer spacing inbetween clay sheet is very less i.e. between 3-5Å. This leads to diffusional constraints for the bulky reactant molecules with greater kinetic diameter due to which most of the acidic sites in the bulk remains unutilized during catalytic processes. The clay materials also cannot be used underhydrothermal condition as catalyst. These materials do not show well crystalline character. Upon heat treatment under hydrothermal condition, the structural collapse as well as extensive hydrolysis of the structure takes place.

1.5 Modification of clay materials

To overcome the above mentioned limitations and to increase the thermal stability, acidity and catalytic properties of clay materials several surface as well as interlayer modifications have been done in past two decades. Most important modifications such as exchange of interlayer cations by inorganic and organic cationic species [1], acid treatment [6], supporting active

species on clay surface for catalysis [10] and pillaring by inorganic polycations [1,6, 9] have been reported in literature. The acidity and the catalytic activity of the clay material can be increased significantly by the first three processes. However multiple advantages in terms of increasing surface area, microporosity, thermal stability, acidity and catalytic activity is obtained by pillaring of clay by inorganic polycations.

1.6 Pillaring of clay by inorganic polycations

Pillared clays are a class of microporous materials studied extensively in the last two decades as catalysts and supports for various organic transformations. These materials are prepared by exchanging the interlayer cations of the clay materials by inorganic polyoxocations [8,9, 11].

Two important properties of clay materials are responsible for pillaring process to occur.

1. *Swelling in polar solvent*: As polar solvent molecules enter into the interlayer spacing of the clay sheet, act as dielectrics and reduce the electrostatic forces between the clay sheets and the interlayer cations resulting in the swelling of the clay sample.

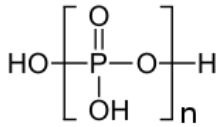
2. *Exchangeability of the interlayer cations*: In the polar solvent, negative charge delocalisation over oxygen plane provides considerable mobility to the interlayer cations which can be exchanged by other cations. Under swelled condition since the interlayer spacing is considerably enhanced, bulkier cationic cluster with typically size in the range of 0.5-2 nm can be inserted inside the clay interlayer. Water molecules enter into the interlayer space of the clay that result in the swelling of these materials. Under such conditions, the inorganic cationic clusters are intercalated into the clay layers by replacing the interlayer cations and giving rise to the intercalated clay [11]. Upon calcination, the inorganic polyoxoclusters are converted into stable oxide clusters that are chemically bonded to the adjacent clay sheets acting as nano-pillars. Clay

pillared with a variety of inorganic polycations of Al, Zr, Ti, Cr, Fe, Ta, V, Ga, Si and Nb are reported in literature[9, 11-18].

1.7 Polyphosphoric acid

Polyphosphoric acid (PPA) is the oligomerised form of the phosphoric acid. A phosphoric acid unit is condensed with another phosphoric acid unit and this process is repeated for maximum ten phosphoric acid units. During each condensation step a water molecule is removed and a hydrogen atom, a phosphorous atom and three oxygen atoms are added. The main skeleton of the polyphosphoric acid comprises of alternating phosphorous and oxygen atoms covalently bonded to each other. The four oxygen atoms are tetrahedral co-ordinated to the centrally located phosphorous atom. A general formula for polyphosphoricacid is $H_{n+2}P_nO_{3n+1}$ where n<10.

2 $H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$



1.8 Objectives of the present study

The main objectives of the present study is to

1. To synthesize various surface and interlayer modified clay materials using zirconia polyoxocations as pillaring agent and polyphosphoric acid as active species.
2. To study the physicochemical characteristics of the synthesized modified clay materials by various analytical techniques such as XRD and UV-Vis, FTIR.
3. To study the catalytic application of the modified clay materials for the synthesis of tetrahydropyridines by multicomponent reaction of ethylacetoacetate, aniline, aryl aldehydes.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

Na-Montmorillonite, $(Na_{0.35}K_{0.01}Ca_{0.02})\ (Si_{3.89}Al_{0.11})^{tet}(Al_{1.60}Fe_{0.08}Mg_{0.32})^{oct}O_{10}(OH)_2.nH_2O$ (Kunipia-F, Kunimine industries, Japan) was used for the preparation of catalysts. The cation exchange capacity of the clay is 120 mequiv $(100g\ clay)^{-1}$. Polyphosphoricacid (PPA), Zirconium oxychloride ($ZrOCl_2.8H_2O$) were procured from Loba Chemie Pvt.Ltd., India. Double distilled water was prepared in the laboratory used in synthesis procedure.

2.1.1 Preparation of PPA-Clay

The PPA polymers are intercalated into the clay sheet in aqueous medium by taking require amount of PPA in aqueous suspension of the clay materials and stirring for the required amount of time following by filtration, washing and drying step.

2.1.2 Preparation of ZrP-PPA clay

5 gm of clay was dispersed in 250 mL of water. The 0.1 M of zirconia pillaring solution was prepared by dissolving required amount of $ZrOCl_2.8H_2O$ salt in 500mL of water. The pillaring solution was subjected to heat treatment at 70°C for 24 hours. The pillaring solution was added dropwise to the clay suspension at the rate of 50 mL per hour under continuous stirring at room temperature. The mixture was left for stirring under room temperature for 24 hours which was subsequently filtered and washed with deionised water to remove the chloride ions. The obtained gel was air dried at 120^0C followed by calcination at 450^0C for two hours to

obtain the Zr-Pillared clay. The as synthesized zirconia pillared clay was dispersed in 200 mL of distilled water. Required amount of PPA was completely dissolved in water. The PPA solution was added dropwise to the ZrP clay slurry under vigorous stirring. Stirring was continued for 12 hours followed by moderate heating and the air drying at 120^0C to obtain the ZrP-PPA clay.

2.2 CHARACTERISATION OF CATALYST MATERIALS:

2.2.1 X-ray diffraction: The X-ray diffraction pattern of the clay material were recorded using a Philips x'pert system X-ray diffractometer using Ni filtered $CuK\alpha_1$ (λ=1.5405 Å) radiation. The XRD measurements were carried out in the 2θ range of 3°-20°C with a scan speed of 2 degrees per minute using Bragg –Brantano configuration.

2.2.2 FTIR spectroscopy: The IR spectra of different clay samples (as KBr pellets) were obtained by using Perkin-Elmer Infrared spectrometer with a resolution of 4 cm^{-1} in the range of 400 cm^{-1} to 4000 cm^{-1}.

2.2.3 UV-Visible spectroscopy: The UV-Visible absorbance spectra of the sample were recorded using Shimadzu spectrometer model 2450 with $BaSO_4$ coated integration sphere in the range of 200-800 nm.

2.3 Catalytic activity study

The catalytic activities of the ZrP-PPA-Clay and PPA-Clay, materials were tested for the synthesis of tetrahydropyridines. The synthesis of tetrahydropyridines was carried out by stirring a mixture of aryl aldehyde (2 mmol), ethylacetoacetate (1 mmol), aniline (2mmol) and 100 mg of different synthesized catalysts in acetonitrile solvent medium at room temperature. The reaction was monitored by TLC. After completion of the reaction, the solid materials was recovered from the ethyl acetate solution and recrystallized from ethanol to acquire the pure product.

CHAPTER 3

Results and Discussions

3.1 XRD study

The XRD diffractograms of the parent clay, Zr-P clay and Zr-P clay calcined have been represented in the fig. 3.1. The parent clay shows an intense peak at $2\theta = 6.8^{o}$. This peak corresponds to the basal spacing which arises due to the reflection from d (001) planes of the clay materials. The calculated value of basal spacing and interlayer spacing was found to be 12.9 Å and 3.3 Å respectively. After intercalation of zirconia oxyhydroxy cations the d_{001} peak is shifted to lower theta values.

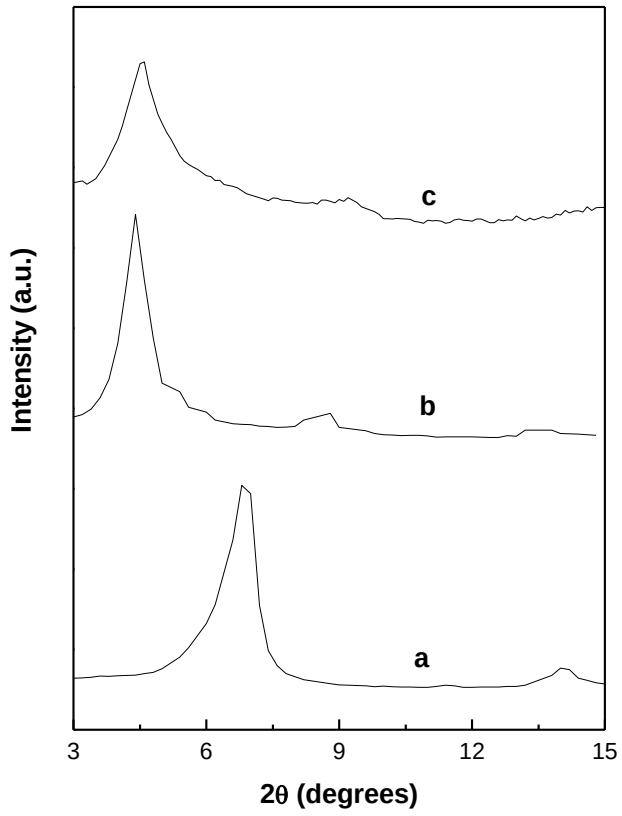


Fig. 3.1 XRD patterns of (a) Clay, (b) Zr-P and (c) Zr-P calcined materials.

These results support for the expansion of the basal as well as interlayer spacings. The basal spacings and the interlayer spacing for the air dried zirconia pillared clay was found to be 20.1 Å and 10.5 Å respectively. The basal and interlayer spacing observed for the calcined Zr-Pillared clay are 19.2 Å and 9.5 Å, respectively. From XRD study it is concluded that the layer spacings and the structure of the zirconia pillared clay material are retained eve after the thermal treatment at 500^{o}C.

3.2 FTIR study

The FTIR spectra of ZrP-PPA, and PPA clay materials along with parent clay have been represented in fig. 3.2. In the stretching region, for the clay materials the bands at 3630 and 3450 cm^{-1} are attributed to the structural hydroxyl groups and water molecules in the interlayer spacings of the clay sheets [13]. These bands are the common feature for the IR spectra for all the above synthesized clay materials. After the intercalation of the PPA to the clay the feature of the IR spectra is altered in the stretching region. For parent clay material another band in bending region is observed at 1630 cm^{-1}. This band is assigned for the bending vibration of the O-H molecules associated with water molecules present in the first co-ordination sphere of the interlayer cations [19]. This band reveals the acidic nature of the clay. This band is quite prominent in all of the FTIR spectra indicating possibility of generation of new acidic sites in the modified clay materials. In the frequency region of 600-1000 cm^{-1} the clay material shows a series of discrete peaks depending upon the cation composition in the octahedral sheet. For parent clay, three bands were observed at 915, 840 and 805 cm^{-1} [13, 19]. These bands have been assigned to the bending vibration modes of Al-Al-OH, Al-Mg-OH and Mg-Mg-OH groups, respectively, in the octahedral layer of the montmorillonite clay.

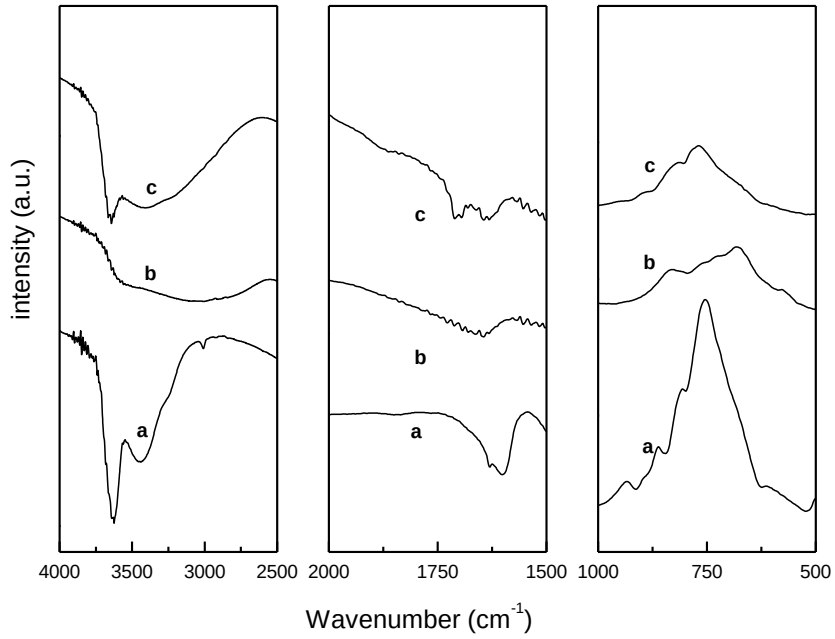


Fig. 3.2 FTIR spectra of (a) Clay, (b) PPA-Clay, (c) ZrP-PPA.

PPA in its bulk state shows a prominent peak at 1010 cm^{-1} due to the stretching vibrations of P-OH bond (figure not shown). The vibrations of P=O and P-O-P bond absorb IR radiation in the range of 1210 cm^{-1} and 890 cm^{-1} respectively [20]. These characteristic peaks with slight shift are observed for the modified clay materials which support the well intercalation of PPA into the clay materials.

3.3 UV-Vis study

The UV-Vis spectra of the parent clay along with different modified clay materials are presented in figure 3.3. The characteristic band of the montmorillonite clay is observed at 247 nm which is assigned to ($Fe^{3+} \leftarrow O^{2-}$, OH^- or OH_2) charge transfer transition for the structural iron present in the octahedral layer of the clay mineral [13]. On intercalation of the Zr-nanopillars into the clay interlayer an alteration in the absorption spectra of the parent clay was observed. For ZrP-PPA

materials, an additional band was observed at 210 nm. This band can be attributed to the $Zr^{4+} \leftarrow O^{2-}$ charge transfer transition from the zirconia nanopillars present in the clay interlayer. In case of ZrP-PPA material, it is likely that extremely small zirconium dioxide nanoclusters exist as pillars with octacoordination in the clay interlayer.

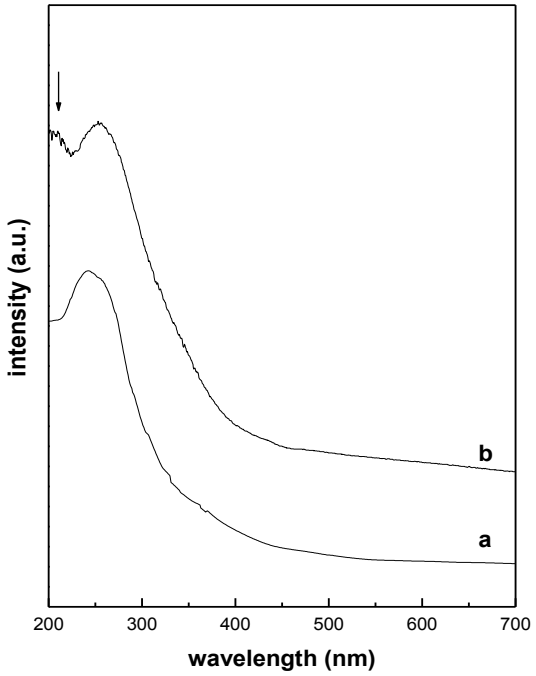
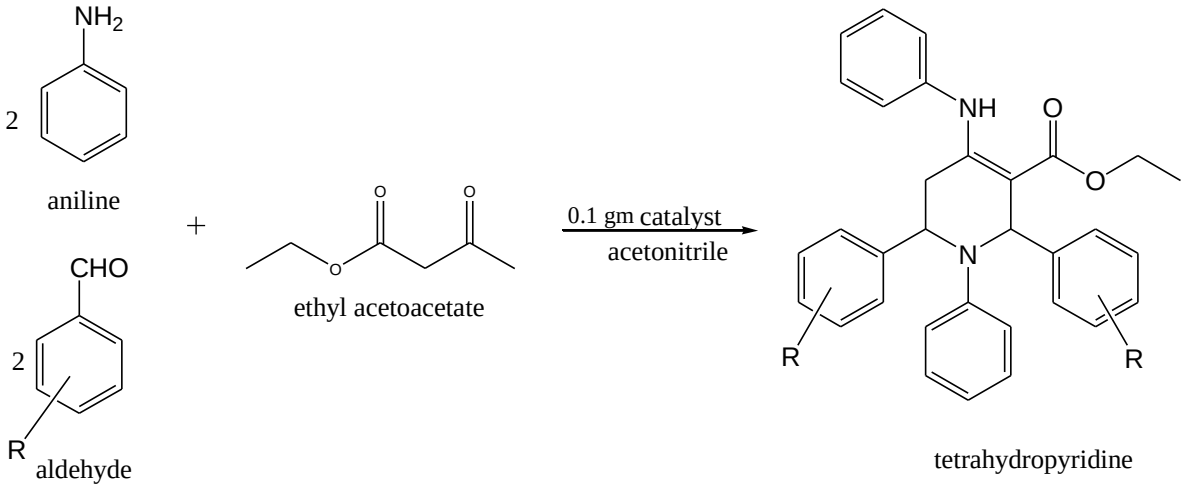


Fig. 3.3. UV-vis spectra of (a) Clay, and (b) ZrP-PPA

3.4 Catalytic studies for Synthesis of tetrahydropyridines.

Tetrahydropyridines skeletal framework comprises of piperdine motifs. These heterocyclic motifs are having significant pharmacological properties. Several past studies show that these motifs are major component of some important medicines such as donepezil, sertindole used for the treatment of Alzheimer's and Schizophrenia diseases [21]. Recent studies show that a variety

of substituted tetrahydropyridines are synthesized using L- proline/TFA, bromodimethylsulfonium bromide (BDMS), tetrabutylammonium tribromide (TBATB), molecular iodine, indiumchloride ($InCl_3$), zirconium oxy chloride ($ZrOCl_2$), ceric ammonium nitrate (CAN) and silica-supported borontrifluoride as catalysts [21-28]. In this present investigation, synthesis of structurally diverse tetrahydropyridines under environment benign condition has been attempted using the modified clay materials as catalysts. Initially, the different clay based materials synthesized in this investigation were studied for their catalytic activity taking the multicomponent condensation of aniline, ethylacetoacetate, aryl aldehydes in acetonitrile medium as model reaction (scheme 3.1).



Scheme 3.1 PPA-ZrP catalyzed synthesis of tetrahydropyridines.

It was observed that the ZrP-PPA materials show better catalytic activity (75% yield) compared to PPA clay. Pure clay was found to be inactive for the reaction. After intercalation of the PPA into the clay lattice, there is a significant improvement in the catalytic activity. The PPA-Clay material shows a yield of 65 %. In order to optimize the protocol for the multicomponent

condensation, the catalyst amount, and reaction stoichiometry were varied. It was observed that for reaction involving 2 mmol aldehyde, 100 mg of the catalyst is ideal for the efficient condensation of the three components. Further increase in the catalyst amount does not have a mark impact on the yield of the product. The optimized molar ratio for the reactants are found to be 2:1:2 for aniline, ethylacetoacetate and aryl aldehydes, respectively. After optimizing the reaction condition, the applicability of the optimized protocol was verified by using different substituted aldehydes in place of benzaldehyde. It has been observed that benzaldehyde substituted by electron withdrawing groups show faster reaction rate and good yield than that of benzaldehyde substituted with electron donating groups. However, under the optimized condition a variety of aldehydes reacted to give the corresponding tetrahydropyridines in high yield and purity. Overall, in this investigation we have developed a new protocol for synthesis of tetrahydropyridines using modified clay catalyst which has many advantages such as high yield and purity of product, mild reaction condition, and recyclable and heterogeneous catalytic process.

CHAPTER 4

CONCLUSION

In this thesis we have reported the structural and interlayer modification of the clay material by intercalating zirconia polyoxocations as pillaring agent and polyphosphoric acid as active species. The physicochemical characteristic of these modified clay materials have been studied using various analytical techniques such as XRD, FTIR, UV-Vis techniques. XRD study signifies the expansion of the interlayer structure on pillaring of zirconia polycations. It also shows that the interlayer structure is retained even after thermal treatment at 500^0C. FTIR and UV-Vis studies indicate the structural integrity of the PPA in the interlayer of the clay materials. The ZrP-PPA intercalated materials have been found to be highly efficient for the multicomponent one pot synthesis of tetrahydropyridines.

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